



Aqueous-phase hydrodechlorination of chlorophenols with pillared clays-supported Pt, Pd and Rh catalysts



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ABSTRACT

Pt, Pd and Rh catalysts supported on pillared clays have been prepared and tested in the hydrodechlorination (HDC) of chlorophenols with H_2 . Different catalyst reduction temperatures, metal loadings and reaction temperatures were tested. Pd and Rh catalysts showed the highest activity with 4-chlorophenol as target compound allowing complete dechlorination at mild operating conditions (25 °C and atmospheric pressure) with negligible metal leaching. The kinetics of 4-CP hydrodechlorination with these catalysts has been analyzed from the corresponding proposed pathways. The stability of the catalysts was checked in long-term experiments being the most stable those of Pd and Rh with no more of 5% activity loss after 300 h on stream. Other chlorophenols (2-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol) were also tested as target pollutants with the Rh catalyst yielding complete conversion in all cases. Chlorinated compounds were not found as final products.

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1. Introduction

Organochlorinated pollutants represent an important environmental concern due to their toxicity. In particular, chlorophenols (CPs) can be found in many ecosystems: surface and ground waters, bottom sediments, air and soils [1]. They are extensively used because of their bactericidal activity, being applied as disinfectants, for the synthesis of pesticides, herbicides and dyes and as preservative agents for wood, paints, fibbers and leather [2]. Most of them have been listed as priority pollutants due to their acute toxicity, resistance to biodegradability and strong bioaccumulation potential [3]. Therefore, their safe disposal has become an important area of research with the ever increasing concern about the environment protection [4]. Different abatement techniques including biological, thermal, and chemical treatments have been developed or studied in the last decade for the detoxification of effluents containing this kind of pollutants [3,5,6]. Catalytic hydrodechlorination (HDC) may be considered as a potential solution since it is a clean, relatively cheap and efficient technique that can be used to treat streams within a wide range of concentrations at ambient or near-ambient temperature [7–9]. The main problem in the use of this process in aqueous phase is the catalyst deactivation, specially caused by the leaching of the metal active phase and the poisoning effect of HCl released upon reaction [10,11].

Different noble metals have demonstrated a fairly good activity [12,13]. Recently, our research group has reviewed the catalysts used for liquid-phase HDC, being activated carbon and alumina the materials most commonly used as catalyst supports [14]. So far clays have been scarcely used for this purpose and, to the best of our knowledge, only by our research group [15–17], although they have received considerable attention for different environmental related applications due to their compatibility, low cost, high selectivity, reusability and operational simplicity [18]. One of the most common modifications made to cationic clay minerals in order to improve their porosity and stability is pillaring, which leads to the formation of a class of materials known as pillared clays (PILCs) [19]. Pillared clays are inorganic layered materials generally prepared by intercalation of metal polyoxocations into smectite clays followed by heat treatment to generate microporous structures where the clay layers are held apart by robust metal oxide pillars. Thirty years ago inorganic polymeric metal ions derived from water-soluble salts of aluminium, zirconium or iron began to be used and they appear among the most widely explored pillaring agents [20]. The resulting pillared clays display sorptive and catalytic properties where the pore size can be adjusted to suit the steric requirements of the guest molecules [21]. Their increased surface area, pore volume, thermal stability and catalytic activity respect to the parent clays make them interesting candidates as catalysts, ion exchangers and adsorbents [22].

It is well known that the method of preparation, the pore structure and morphology of the support, as well as its interaction with the active phase may greatly influence the catalytic activity in different processes. Pd has been the most commonly used active phase

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for liquid-phase HDC studies with more than 50% of literature share. Ni is represented in around 15% being Pt and Rh less studied [14]. Pillared clays supporting different metals have been used in several hydrogenation reactions: Rh for acetone [23] or quinoline [24], Pt for adipic ester [25] and Ru for dimethyl adipate [26].

In previous papers we have reported that precious metals supported on pillared clays showed high and stable activity in the HDC of 4-chlorophenol (4-CP) using formic acid as hydrogen source [15–17]. A preliminary study on the direct use of hydrogen for the HDC of 4-CP was also performed using Rh-pillared clays catalysts [17], always in batch mode. Following those studies the aim of the current work is to test pillared clays-supported Pt, Pd and Rh catalysts in the HDC of chlorophenols in aqueous solution using direct hydrogen. The activity of those catalysts was checked in batch mode, testing the effect of reaction temperature and metal loading with 4-CP as target compound. The kinetics of the process has been analyzed. The effect of the reduction temperature used in the preparation of the catalysts as well as their stability in continuous long-term experiments has been also studied. Likewise, other chlorophenols were tested as target compounds with the catalyst that showed the highest activity in the HDC of 4-CP.

2. Experimental

2.1. Preparation of the catalysts

The catalysts prepared consisted of Pt, Pd and Rh supported on pillared clays. The starting material used to prepare the pillared clays was a purified-grade bentonite supplied by Fisher Scientific Company (Loughborough, OR, USA). The chemical analysis (wt%) of this bentonite was: SiO₂, 52.22; Al₂O₃, 16.81; Fe₂O₃, 3.84; Na₂O, 1.26; MgO, 0.88; CaO, 0.74; K₂O, 0.80. The cation-exchange capacity (CEC) was 97 mequiv. per 100 g of clay. Al-pillared clay (Al-PILC) was obtained following the method described elsewhere [16] although the salt of Al employed in the current work was Al(NO₃)₃ instead of the previously used AlCl₃.

The metallic active phase, Pt, Pd or Rh, was introduced into the Al-PILC structure by wet impregnation from H₂PtCl₆ solution (8 mass% of Pt), PdCl₂ or RhCl₃, respectively. In the case of Pd and Rh, the corresponding precursors were dissolved in 0.1 M HCl and 0.2 M HCl, respectively, due to their low water solubility. Catalysts with metal loads amid 0.5 and 3 wt% were prepared. After impregnation, the wet solid was dried for 2 h at room temperature, 14 h at 110 °C and calcined in air atmosphere for 2 h at 500 °C with a heating ramp of 2 °C/min during 4 h. The particle fraction lower than 100 µm was separated by sieving and reserved for HDC experiments. Prior to use the catalysts were reduced in situ under continuous H₂ flow (35 N mL/min) at different temperatures (90–400 °C) during 2 h. The catalysts were named by the metal followed by its nominal percent load and the reduction temperature. So, for example, Pt-1-90 refers to catalyst with 1 wt% Pt reduced at 90 °C. When previous reduction was not accomplished, only the metal symbol and percent load were used.

2.2. Characterization methods

The porous structure of the pillared clays and the catalysts was characterized from the N₂ adsorption–desorption isotherms, obtained at 77 K using a Micromeritics Tristar 3000 apparatus. The samples were previously outgassed at 160 °C and 5 × 10^{−3} Torr for 16 h. Specific areas were obtained according to BET method. The metal content in the catalysts was measured by Total-reflection X-ray fluorescence with a TXRF EXTRA-II (Rich & Seifert, Germany) spectrometer after digestion of the solid samples by acid treatment (nitric, hydrochloric and sulphuric acids mixture) at 100 °C.

The particle size distribution of the metallic phase was determined by transmission electron microscopy (TEM) using a JEOL 2100F microscope with a point resolution of 0.19 nm coupled with an energy-dispersive X-ray spectrometer (EDXS; INCA x-sight, Oxford Instruments) used for elemental analysis. The STEM images were obtained using a Philips XL30 coupled with EDX (EDAX DX4i).

In addition, X-ray photoelectron spectroscopy (XPS) was used to analyze the surface composition of the catalysts by means of a VG Escalab 200R spectrometer, MgKα ($h\nu = 1253.6$ eV). The peaks were fitted by a non-linear least square fitting programme using a properly weighted sum of Lorentzian and Gaussian component curves after background subtraction according to Shirley. The binding energies and atomic concentrations of the samples were calculated from the XPS results of total integrated peak areas.

A Micromeritics ChemiSorb 2705 pulse analyzer was used to determine the metal dispersion of the catalysts by CO chemisorption at 25 °C. The sample (0.1 g) was first cleaned with helium and then reduced at 90, 200 or 400 °C for 2 h under hydrogen flow (20 N mL/min). Then, it was cooled under helium flow up to 25 °C and several pulses of CO were then introduced until saturation of the catalyst surface was achieved.

2.3. HDC experiments

The hydrodechlorination experiments were carried out in batch mode in jacketed stoppered glass reactors under continuous stirring at atmospheric pressure. After stabilization of temperature the corresponding amount of catalyst (1 g) was added to 1 L of an aqueous 4-CP solution (100 mg/L) and stirring was maintained for 15 min. Then, hydrogen was fed to the reactor at a continuous flow rate of 50 N mL/min. Samples were withdrawn at 15, 30 min and each hour until completing 4 h. In the experiments where the initial reaction rate was measured, samples were taken every 2 min for the first 10 min of reaction. The catalyst was separated by filtration using 0.45 µm pore size PTFE filters. Internal and external mass transfer limitations were discarded in our working conditions after some preliminary experiments where the effect of stirring velocity and particle size was checked.

The stability of the catalysts was tested in 100–300 h continuous mode experiments in a fixed-bed reactor (Pyrex glass, 30 cm length, 9 mm internal diameter). The catalyst (0.1 g) with particle size <100 µm was mixed with glass beads of 2 mm external diameter in order to avoid channelling. The 100 mg/L 4-CP aqueous solution was fed at 0.42 mL/min flow rate, so that the space-time was 5.1 kg_{cat} h/mol. The H₂ flow used was 1 N mL/min. Liquid samples were periodically taken from the reactor exit upon the time on stream.

The concentrations of 2-chlorophenol (2-CP), 4-CP, 2,4-dichlorophenol (2,4-DCP) and phenol were measured by HPLC with a diode-array detector (Prostar, Varian) using a C₁₈ column as stationary phase (Valco Microsorb-MW 100-5C₁₈) and a mixture of acetonitrile and water (1:1, v/v) as mobile phase. 2,4,6-trichlorophenol (2,4,6-TCP) and the other reaction products identified (cyclohexanone (c-one), cyclohexanol and 2,6-dichlorophenol (2,6-DCP)) were analyzed by means of a GC/FID (GC 3900 Varian) using a 30 m length and 0.25 mm i.d. capillary column (CP-Wax 52 CB, Varian) and nitrogen as carrier gas. Replicates of the reactions yielded data reproducibility better than ±5%. The repeatability of the analyses was ±3% in the case of HPLC and ±5% for GC/FID.

3. Results and discussion

3.1. Characterization of the catalysts

Table 1 summarizes the textural characteristics and the as measured metal load of the catalysts. The Al-PILC showed higher basal

Table 1
Characterization of the starting materials and the catalysts prepared.

Catalysts	Surface area (m ² /g)	External area (m ² /g)	Micropore volume (cm ³ /g)	Metal load (wt%)
Bentonite	35	24	0.005	–
Al-PILC	212	37	0.096	–
Pt-0.5	195	68	0.060	0.48
Pt-1	178	66	0.056	1.02
Pt-3	171	64	0.053	3.05
Pd-0.5	173	52	0.063	0.52
Pd-1	172	57	0.053	1.00
Pd-3	149	46	0.051	2.94
Rh-0.5	185	39	0.089	0.51
Rh-1	164	36	0.083	0.98
Rh-3	155	43	0.070	2.97

spacing (not shown) and surface area values than the starting bentonite, indicating a successful pillaring process. As can be seen the BET surface area decreased upon impregnation as the metal load increased. All the catalysts showed a moderately significant contribution of mesoporosity as revealed the values of external or non-microporous surface area compared with those of the BET surface area.

TEM images of the catalysts with 1% metal load are shown in Fig. 1. The Pt catalyst yielded metal particles of around 10–40 nm in contrast with Pd (5–15 nm) and most in particular Rh which showed frankly small particles (2–3 nm). Whereas Pd and Rh particles look more or less spherical, in the case of Pt a polyhedral shape is observed. Therefore, to determine the size of Pt particles is not easy and several authors have reported different ways of considering these polyhedral particles. Whereas Kanda et al. [27] assumed a spherical shape other authors give a “caliper” diameter, i.e., the average of two diameters corresponding to the largest sphere inside the particle and to the smallest sphere entirely covering the particle, which has showed a good agreement with the particle sizes measured by the Scherrer expression from DRX [28]. The most commonly assumed procedure to calculate the size of this kind of particles consists in measuring the lower internal diagonal, as it has been reported by Long et al. [29].

3.2. Hydrodechlorination of 4-CP

3.2.1. Effect of the catalyst reduction temperature

Fig. 2 shows the results obtained from 4-CP HDC with the catalysts reduced at different temperatures. Those with non-reduced catalysts are also included. Looking at these last, Rh shows a substantially higher activity than the two other metals, most in particular than Pt. This ranking of activity follows the decreasing order of metal particle size of the catalysts shown in Fig. 1.

Reduction at moderate temperatures (90 and 200 °C) produces a beneficial effect on the catalytic activity whereas increasing that temperature up to 400 °C has a dramatic detrimental effect in the activity of Pt and Pd. In the case of Rh that effect is much lower and the activity still remains above that of the non-reduced catalyst. These results can be explained on the basis of a loss of metal dispersion (see Table 2) most probably due to aggregation upon thermal treatment. Sinterization of Pd particles under thermal treatment has been previously reported in the case of Pd/alumina catalysts [12]. In our case that can be observed in Fig. 3 which shows TEM micrographs of the Pd catalyst reduced at 200 and 400 °C. In the case of Rh the effect is much less important because of the substantially lower metal particle size, which even with some aggregation after heating at 400 °C remains significantly below than for the two other metals.

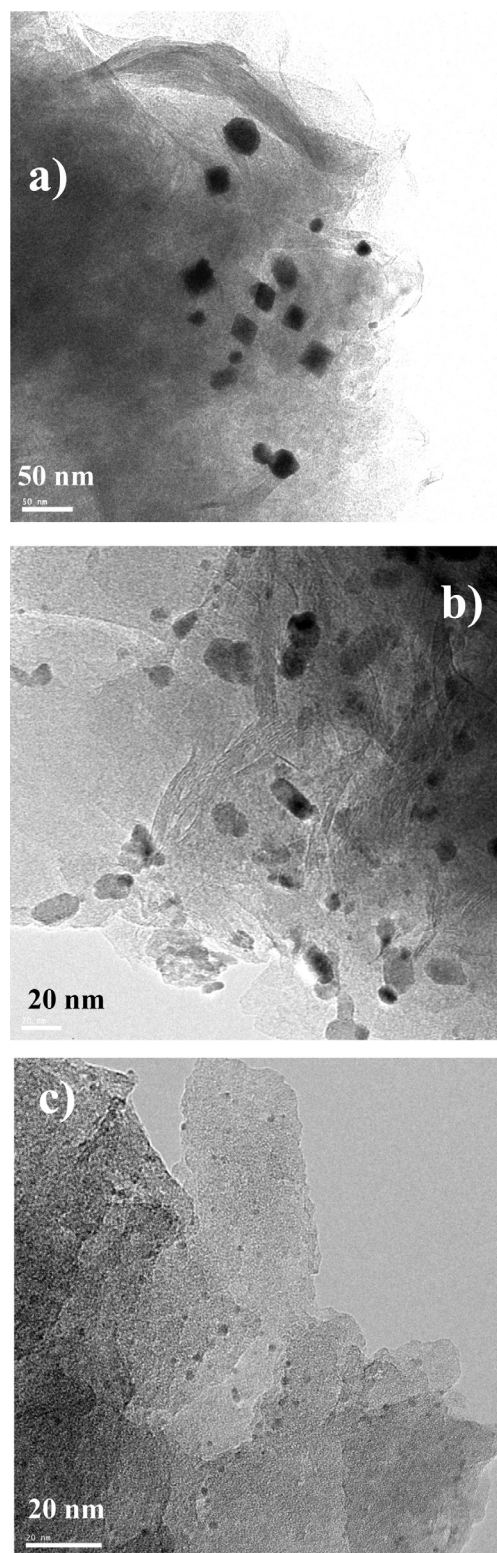


Fig. 1. TEM images of (a) Pt-1, (b) Pd-1 and (c) Rh-1 catalysts.

The particularly high HDC activity of the Rh catalyst prereduced at moderate temperature can be consistently associated to the very good metal dispersion which can be better observed in Fig. 4 showing a Cs-corrected STEM-HAADF image of the Rh-1 catalyst reduced at the lowest temperature tested (90 °C). A frankly homogeneous distribution of small Rh particles is clearly seen.

Table 2

Metal dispersion (CO chemisorption) and initial rate and TOF values for 4-CP HDC with the fresh and reduced catalysts.

Catalysts	Metal dispersion (%)	k (L min ⁻¹ g _{metal} ⁻¹)	Initial rate (mmol min ⁻¹ g _{metal} ⁻¹)	TOF × 10 ² (s ⁻¹)
Pt-1	10.5	0.17 ± 0.02	0.13	0.40
Pt-1-90	10.8	0.54 ± 0.02	0.42	1.26
Pt-1-200	15.0	0.41 ± 0.02	0.32	0.69
Pt-1-400	6.3	0.07 ± 0.01	0.06	0.31
Pd-1	7.7	1.41 ± 0.13	1.10	2.53
Pd-1-90	8.3	7.58 ± 0.44	5.90	12.61
Pd-1-200	10.2	3.64 ± 0.53	2.83	4.92
Pd-1-400	4.7	0.44 ± 0.02	0.34	1.28
Rh-1	19.0	2.68 ± 0.28	2.09	1.89
Rh-1-90	22.0	15.24 ± 0.91	11.86	9.25
Rh-1-200	24.0	18.74 ± 2.49	14.59	10.43
Rh-1-400	17.0	3.57 ± 0.29	2.78	2.80

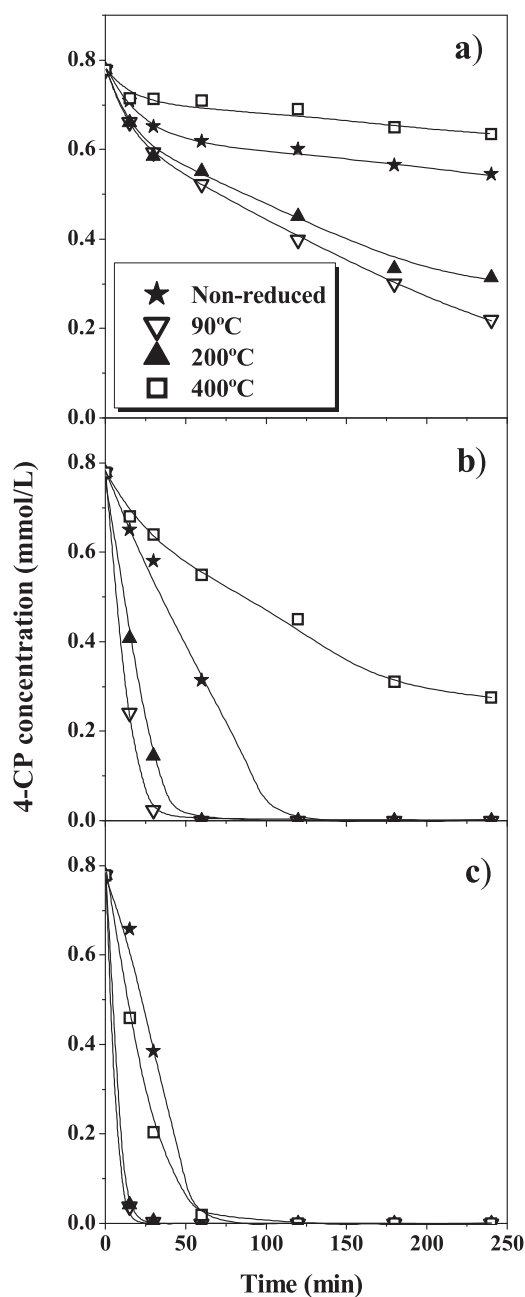
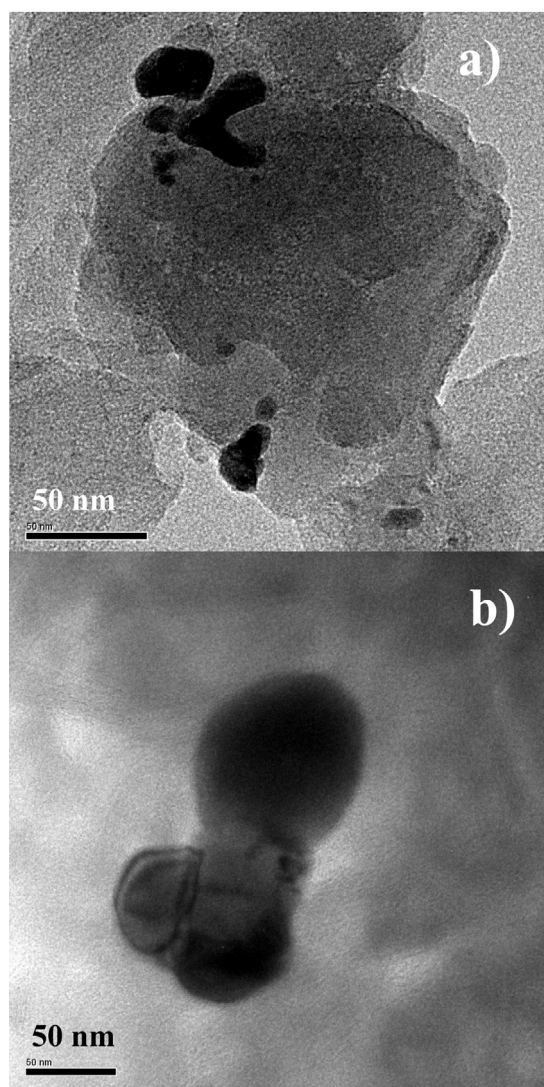
**Fig. 2.** HDC of 4-CP at 25 °C with the Pt-1 (a), Pd-1 (b) and Rh-1 (c) catalysts reduced at different temperatures (0.1 g/L initial 4-CP, 1 g/L catalyst).**Fig. 3.** TEM images of Pd-1-200 (a) and Pd-1-400 (b).

Table 2 reports the dispersion values obtained from CO chemisorption. These values confirm the improved dispersion of the metal active phase upon reduction at moderate temperature (90–200 °C range) followed by a significant decrease when the reduction temperature was raised up to 400 °C. As can be seen, the highest dispersion values correspond to the Rh catalysts, confirming the TEM results. Likewise, in Table 2 are collected the values

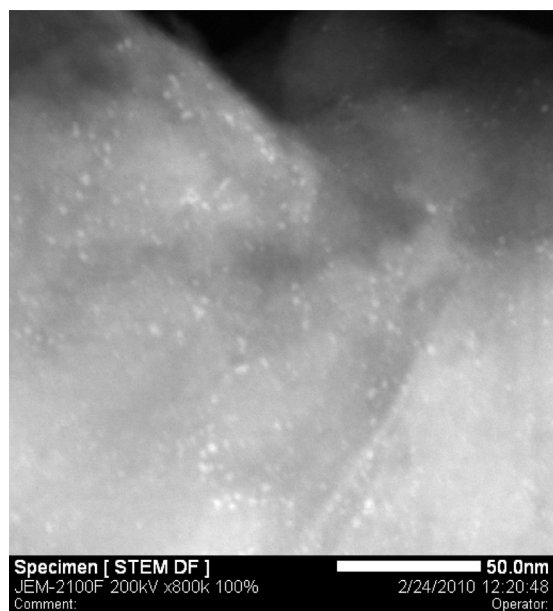


Fig. 4. Cs-corrected STEM-HAADF image of Rh-1-90.

of TOF calculated from initial rates which are also included in the table. The TOF values have been calculated as:

$$\text{TOF}(\text{s}^{-1}) = \frac{r_0 \cdot M_A \cdot 10^{-3}}{D \cdot 60} \cdot 100 \quad (1)$$

where r_0 represents the initial rate (see Table 2 for units), D the metal dispersion (%) and M_A the atomic mass of the corresponding metal (g/mol). Initial rate values were obtained from those of rate constants (Table 2) resulting from the kinetic study later described.

As can be seen in Table 2, the highest TOF value among the fresh (non-reduced) catalysts was yielded by the Pd one ($2.53 \times 10^{-2} \text{ s}^{-1}$) indicating the high activity of this metal for this process even without prior reduction. Among the reduced catalysts, those reduced at moderate temperatures (90–200 °C) yielded the highest initial rates and TOF values. The Pd catalyst, with only 1 wt% of this metal, showed TOF values comparable to those reported in the literature for HDC of aqueous 4-CP with carbon-supported Pd catalysts (5 wt%) ranging between 0.05 s^{-1} and 0.14 s^{-1} [30,31] and Pd catalysts supported on mesoporous silica–carbon nanocomposites or activated carbon (0.015 – 0.42 s^{-1}) at reaction temperatures between -15 °C and 40 °C [9].

Reduction at 400 °C led to a decrease of TOF in agreement with the observed by other authors that related this decrease with the higher metallic particle sizes at that reduction temperature [32]. In order to analyze this result more in depth the effect of the oxidation state of the metallic active phase was investigated. XPS analyses of the catalysts reduced at different temperatures were carried out and the ratio of zerovalent to electrodeficient metallic species was obtained. The values are collected in Table 3 (see XPS spectra in Figure S1 of the Supplementary data). The relative occurrence of zerovalent metal increased with the reduction temperature and at 400 °C the metallic phase was completely reduced to the zerovalent state. Thus, the presence of electrodeficient metallic species in addition to the zerovalent ones seems to improve the HDC activity. This conclusion has been previously reported by other authors working with Pd catalysts supported on activated carbon [33], silica [34] or TiO_2 [35].

Fig. 5 shows the results from 4-CP HDC with the catalyst tested at different metal loads within the range of 0.5 – 3 wt%. The catalysts were reduced at 90 °C in all cases. Firstly, TXRF analyses of the HDC effluents showed the absence of metal leaching thus

Table 3

Relative occurrence of metallic species in the catalysts reduced at different temperatures and after use in 4-CP HDC.

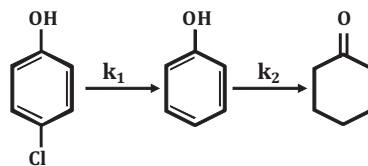
	$\text{Me}^0 / (\text{Me}^0 + \text{Me}^{n+}) (\%)$
Pt-1	57
Pt-1-90	67
Pt-1-200	100
Pt-1-400	100
Pt-1-90 used	68
Pd-1	45
Pd-1-90	52
Pd-1-200	66
Pd-1-400	100
Pd-1-90 used	53
Rh-1	0
Rh-1-90	36
Rh-1-200	60
Rh-1-400	100
Rh-1-90 used	46

indicating the stability of the catalysts on that respect. The carbon balance was matched between 90% and 100% and almost 100% closure was achieved for chlorine.

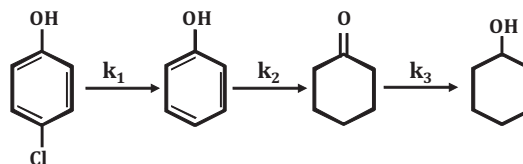
As can be seen, the rate of 4-CP disappearance was substantially increased in all cases with the precious metal load. This is consistent with the increase of the amount of exposed metal, whose values are summarized in Table 4. As seen before, the Pt catalysts showed by far the lowest activity. At 0.5 metal load only 50% 4-CP conversion was achieved after 4 h reaction time whereas Pd and Rh allowed complete conversion in about one-half that time. As can be seen in Table 4, the values of exposed metal are fairly similar for the Pt and Pd catalysts at 0.5 nominal metal loading whereas dechlorination of 4-CP proceeds much faster with the second. Phenol, cyclohexanone and cyclohexanol were the reaction products with Pt and Rh catalysts, whereas in the case of Pd cyclohexanol was not detected, indicating a lower activity for further hydrogenation following dechlorination. This is in agreement with previous works [36,37]. The Rh catalysts allowed the fastest 4-CP conversion and a more in-depth further hydrogenation giving rise to cyclohexanol as the only reaction product. Increasing the metal load led to a deeper hydrogenation in all cases. The highest rate of 4-CP dechlorination yielded by the Rh catalyst can be explained by the higher values of exposed metal. Nevertheless, looking at the specific activity of the three metals, the initial TOF values were higher for the Pd catalysts, despite their lower amount of exposed metal, proving their great dechlorination activity.

From the curves of Fig. 5, the following reaction pathways can be proposed:

Pd catalyst



Pt and Rh catalysts



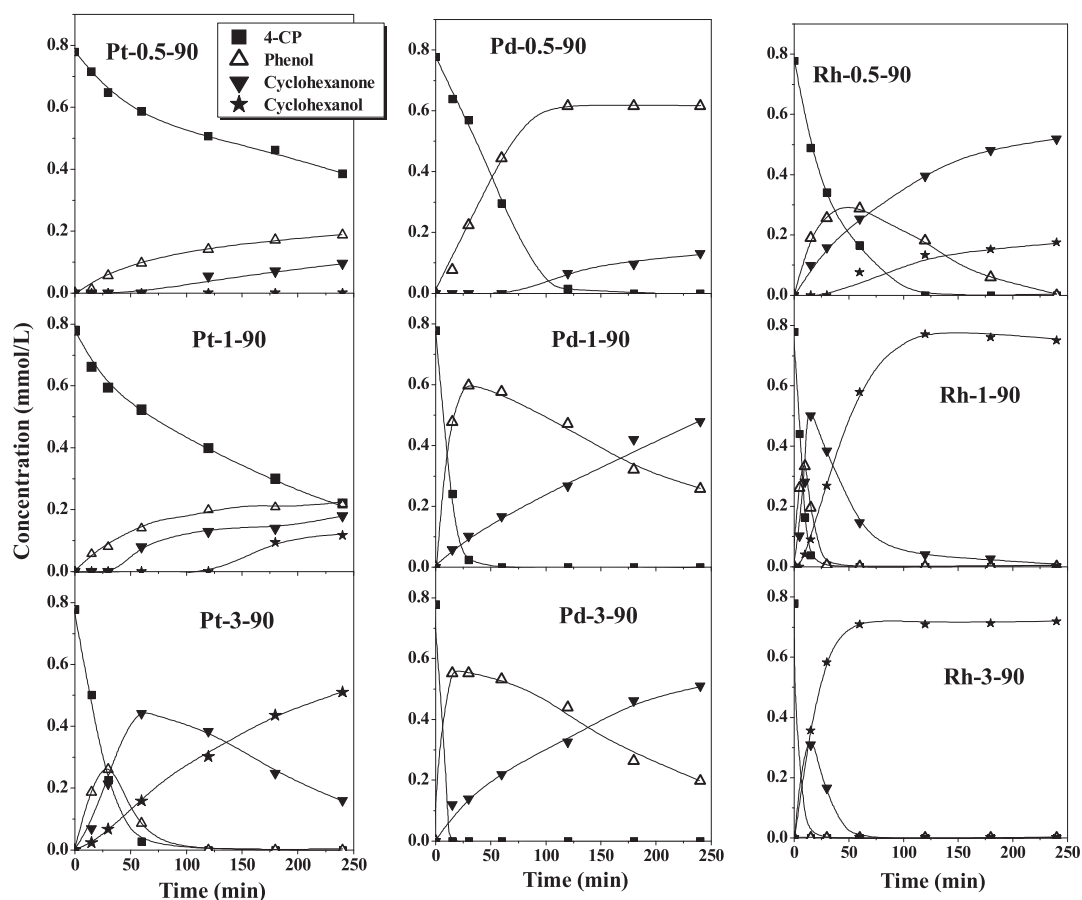


Fig. 5. HDC of 4-CP with catalysts of different metal loads (25 °C, 0.1 g/L initial 4-CP, 1 g/L catalyst).

Table 4

Values of metal dispersion (CO chemisorption) and initial rates, exposed metal and TOF values for 4-CP HDC at different metal loadings.

Catalysts	Metal dispersion (%)	Initial rate (mmol min ⁻¹ g _{metal} ⁻¹)	Exposed metal (μmol g _{catalyst} ⁻¹)	TOF × 10 ² (s ⁻¹)
Pt-0.5-90	5.0	0.46	1.23	2.99
Pt-1-90	10.8	0.42	5.65	1.26
Pt-3-90	3.9	0.94	6.10	7.84
Pd-0.5-90	2.1	2.35	1.02	19.8
Pd-1-90	8.3	5.90	7.80	12.6
Pd-3-90	7.4	3.78	20.4	9.06
Rh-0.5-90	23.5	3.91	11.6	2.85
Rh-1-90	22.0	11.9	20.9	9.25
Rh-3-90	11.7	5.65	33.8	8.28

On the basis of these reaction schemes, the following rate equations can be written based on the assumption of pseudo-first order kinetics:

$$R_{4-CP} = \frac{dC_{4-CP}}{dt} = -r_1 = -k_1 C_{4-CP} \quad (2)$$

$$R_{phenol} = \frac{dC_{phenol}}{dt} = r_1 - r_2 = k_1 C_{4-CP} - k_2 C_{phenol} \quad (3)$$

$$R_{C-one} = \frac{dC_{C-one}}{dt} = r_2 = k_2 C_{phenol} \quad (\text{Pd catalyst}) \quad (4)$$

$$R_{C-one} = \frac{dC_{C-one}}{dt} = r_2 - r_3 = k_2 C_{phenol} - k_3 C_{C-one} \quad (\text{Pt and Rh}) \quad (5)$$

$$R_{cyclohexanol} = \frac{dC_{cyclohexanol}}{dt} = r_3 = k_3 C_{C-one} \quad (\text{Pt and Rh}) \quad (6)$$

The concentration–time curves for the catalysts at 1 wt% metal load were fitted to the above equations by a nonlinear regression programme using the Marquardt algorithm at the 95% probability level. Table 5 summarizes the values obtained for the kinetic constants at 25 °C.

Table 5

Values of the kinetic constants for 4-CP HDC at 25 °C.

Catalyst	Kinetic constant	k (L min ⁻¹ g _{metal} ⁻¹)	r^2
Pt-1-90	k_1	$5.4 \times 10^{-1} \pm 2.0 \times 10^{-2}$	0.992
	k_2	$7.9 \times 10^{-1} \pm 7.0 \times 10^{-2}$	
	k_3	$6.0 \times 10^{-1} \pm 9.0 \times 10^{-2}$	
Pd-1-90	k_1	7.6 ± 0.4	0.994
	k_2	$4.8 \times 10^{-1} \pm 2.0 \times 10^{-2}$	
Rh-1-90	k_1	15.2 ± 0.9	0.991
	k_2	14.7 ± 1.1	
	k_3	3.3 ± 0.2	

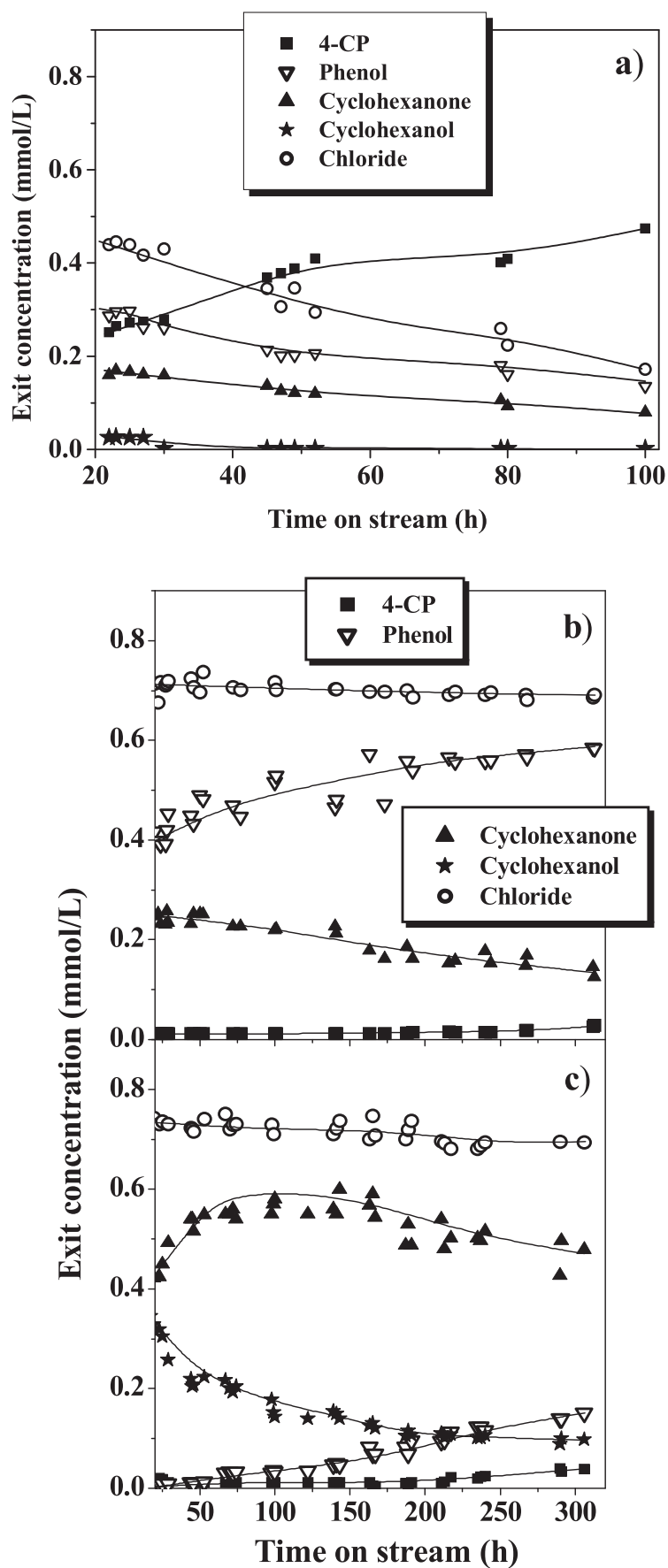


Fig. 6. Long-term experiments of 4-CP HDC with (a) Pt-1-90, (b) Pd-1-90 and (c) Rh-1-90 (25 °C, space-time: 5.2 kg_{cat} h/mol).

Table 6Values of the k_1 kinetic constant for 4-CP HDC at different temperatures.

Catalyst	Temperature (°C)	k_1 (L min ⁻¹ g _{metal} ⁻¹)	r^2
Pt-1-90	25	$5.4 \times 10^{-1} \pm 2.0 \times 10^{-2}$	0.992
	35	$6.2 \times 10^{-1} \pm 3.0 \times 10^{-2}$	0.988
	40	$9.8 \times 10^{-1} \pm 1.0 \times 10^{-2}$	0.962
	50	3.0 ± 0.3	0.964
Pd-1-90	25	7.6 ± 0.44	0.994
	35	10.9 ± 1.1	0.990
	40	21.0 ± 4.7	0.993
	50	23.6 ± 5.9	0.996
Rh-1-90	25	15.2 ± 0.9	0.991
	35	16.3 ± 0.9	0.992
	40	21.5 ± 1.2	0.994
	50	28.7 ± 3.0	0.987

Whereas with Pt the rate constants for the dechlorination and further hydrogenation steps are fairly similar, in the case of Pd dechlorination proceeds significantly faster than hydrogenation of the resulting primary product, phenol. On the other hand, the Rh catalyst, the most active one, yielded similar values of the dechlorination and phenol hydrogenation rate constants whereas formation of cyclohexanol from cyclohexanone occurred at a lower rate. Similar trends have been reported in previous works on 4-CP HDC with analogous catalysts based on these three precious metals but supported on γ -alumina [13,36].

The values of k_1 (4-CP disappearance) at different temperatures within the 25–50 °C range are given in Table 6. From them the corresponding values of apparent activation energy were calculated by the Arrhenius equation. Values of 56 ± 11 ; 39 ± 9 and 21 ± 5 kJ/mol were obtained for the Pt, Pd and Rh catalysts, respectively. Shindler et al. [38] reported a value of 24.8 kJ/mol with Pd on activated carbon (Pd/AC) within the 30–85 °C range. Also for Pd/AC Yuan and Keane [39] obtained 41.2 kJ/mol (0–30 °C). Diaz et al. [13] gave 47, 51 and 58 kJ/mol for Pd/Al₂O₃, Rh/AC and Pt/AC, respectively. Jin et al. [9] found activation energy values of 15.6 and 40.8 kJ/mol with a 5 wt% Pd catalysts supported on mesoporous silica–carbon nanocomposites and activated carbon, respectively, both within the range of –15 to 40 °C. Felis et al. [40] found a value of 45 kJ/mol working in the range of 40–80 °C with a 4.53 wt% Ru/C catalyst.

3.2.2. Stability tests

For the sake of learning on the stability of the catalysts, long-term (100 and 300 h) continuous experiments of 4-CP HDC were carried out as detailed in Section 2. The results are depicted in Fig. 6. The Pt catalyst showed a progressive loss of dechlorination activity as can be seen from the evolution of the exit concentrations of 4-CP and chloride. On the opposite, the Pd and Rh showed a frankly stable performance in terms of dechlorination although a decay of activity was observed for further hydrogenation. Metal leaching along the experiments was negligible in all cases and, therefore, metal loss from the catalysts can be discarded as a cause of deactivation.

With the three catalysts the amount of chloride measured in the liquid phase was somewhat unbalanced with respect to the extension of 4-CP dechlorination. Thus, small amounts of chloride and/or chlorine-bearing species may be accumulating on the catalyst surface which could cause deactivation. To check this, XPS analyses of the used catalysts were carried out and the results are summarized in Table 7 (see XPS profiles in Figure S2 of the Supplementary data). The chlorine content of the Pt catalyst is higher than that of Pd and Rh, corresponding almost 60% to organic chloride, which can be attributed to the adsorption of chlorinated organic species.

A decrease of the BET surface area of the catalysts was observed after the long-term experiments. That decrease was more pronounced in the Pt catalyst accounting up to 45%, whereas for Pd and Rh 35 and 25% reduction, respectively, was observed.

Table 7

Atomic surface percentages of organic chloride in the used catalysts after long-term experiments measured by XPS.

Catalyst	Cl 2p (%)	Organic Cl (%)	Zerovalent to electrodeficient species ratio ^a
Pt-1-90 used	0.33	0.19	2.1
Pd-1-90 used	0.23	0.11	1.1
Rh-1-90 used	0.25	0.09	0.9

^a From data in Table 3.

3.3. HDC of other chlorophenols

Hydrodechlorination of 2-CP, 2,4-DCP and 2,4,6-TCP with the Rh catalyst was investigated and the results are depicted in Fig. 7. Complete dechlorination was achieved in all cases. The main reac-

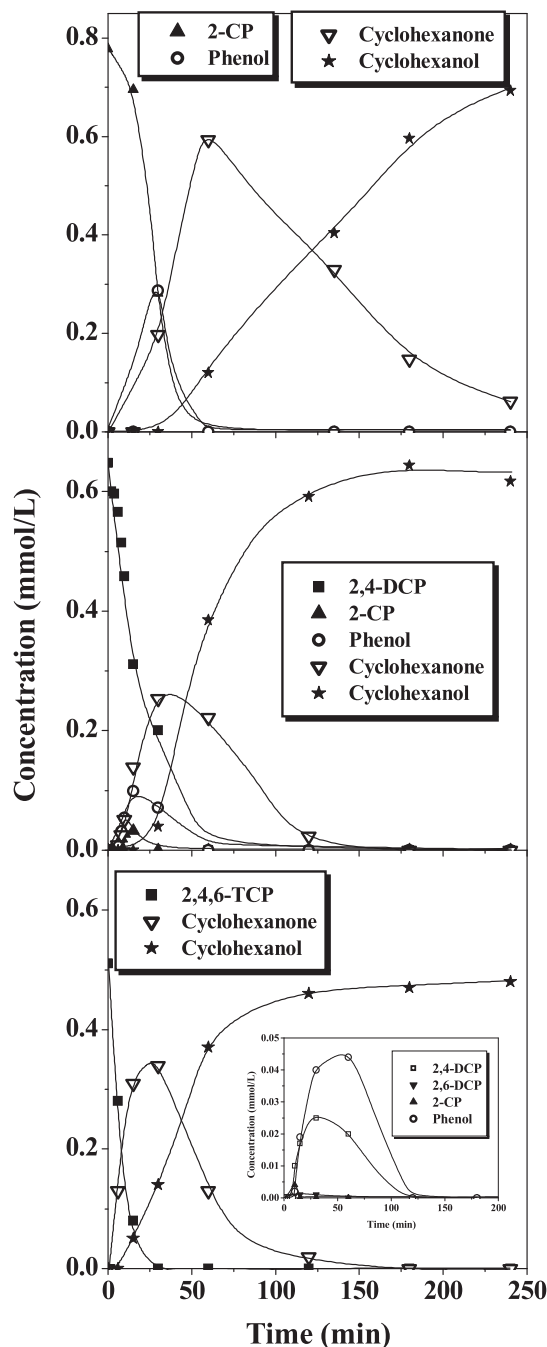


Fig. 7. HDC of different chlorophenols with Rh-1-90 catalyst (25 °C, 0.1 g/L initial reactant, 1 g/L catalyst).

tion product was cyclohexanol, being phenol and cyclohexanone reaction intermediates. In the case of 2,4-DCP, 2-CP was detected at very low reaction times as well as 2-CP, 2,4-DCP and 2,6-DCP in the case of 2,4,6-TCP. Those chlorinated intermediates disappeared completely in less than 2 h reaction time. Except in the case of 2-CP HDC cyclohexanol was by far the main reaction product after complete dechlorination, with very small amounts of cyclohexanone which finally was completely converted into cyclohexanol. This last compound has a low ecotoxicity (EC_{50} : 114 mg/L), thus indicating that the Rh catalyst can provide an effective detoxification of effluents containing chlorophenols. Carbon and chlorine balances were matched at more than 90 and 100%, respectively.

4. Conclusions

Own-prepared Pt, Pd and Rh catalysts supported on pillared clays have been prepared and tested as catalysts for the hydrodechlorination of chlorophenols. Reduction at moderate temperature (90–200 °C) under H_2 atmosphere improves the activity of the catalysts. Rh showed the highest dechlorination activity and gave rise to a deeper hydrogenation up to cyclohexanol, which has a very low ecotoxicity. Long-term experiments revealed a high stability of the Pd and Rh catalysts whereas Pt suffered relatively rapid deactivation, most probably due to the adsorption of chlorinated species. The Rh catalyst allowed complete dechlorination of di- and tri-chlorophenols giving rise to cyclohexanol as final reaction product.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2013.11.010>.

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